I. POLYMERIC COORDINATION COMPLEXES WITH AMINO ACIDS

II. UREA-FORMALDEHYDE POLYMERS

BY

JOHN RAYMOND ELLIOTT

B.S., Iowa State College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

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PART I. POLYMERIC COORDINATION COMPLEXES WITH AMINO ACIDS

Introduction

α-Amino acids and metal cations which are capable of forming coordination compounds react to give inner or non-ionic complexes. These compounds have been characterized by high stability, low solubility, and have been colored.[1,2,3] Amino acids containing two *alpha* or *ortho* amino acid groups should form inner complexes which are either linear or network polymers depending on the coordination number of the cation.

Discussion

The complex coordination compounds of cobaltic, nickelous, chromic, cupric, and ferrous ions with α,α'-diaminosebacic acid, methylene-bis-(4-amino-3-benzoic acid), and 3,3′-benzidene disulfonic acid have been investigated.

Cobalt formed a deep brown complex with methylene-bis-aminobenzoic acid and a lavender complex with diaminosebacic acid. The composition of these complexes indicated that they had a polymeric network structure composed of two cobaltic ions per three amino acid residues. They were insoluble in organic solvents and only slowly attacked by inorganic acids and bases. Cobalt did not form a complex with benzidene disulfonic acid.

Chromium formed a grey-blue complex with diaminosebacic acid that was only slowly attacked by acids and bases. The composition indicated that it was polymeric in nature. With methylene-bis-aminobenzoic acid the complex was violet in color. The composition indicated, however, that extensive hydrolysis of the complex had taken place.

Nickel formed pale blue complexes with diaminosebacic acid and methylene-bis-aminobenzoic acid. Their composition indicated that they had a linear polymer structure and that some ammonia was also coordinated to the nickel.

Copper formed a blue complex with diaminosebacic acid and a green complex with methylene-bis-aminobenzoic acid. They were rather unstable in the presence of inorganic acids and bases. Their composition indicated that one molecule of copper was associated with two molecules of amino acid and hence were monomeric. Copper formed an unstable, yellow complex with 3,3′-benzidene disulfonic acid. The composition of this complex indicated that it was polymeric.

No complexes of ferrous ion with the above amino acids could be prepared.

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PART II. UREA-FORMALDEHYDE POLYMERS

Introduction

The structures proposed for the urea-formaldehyde resins by previous investigators have been based in part on the view that urea is a diamide and as such, reacts with formaldehyde to yield methylol and methylene-bis-amides.[1,2] Urea may behave as an amino acid amide, however, in its reaction with formaldehyde. Amines are known to react with formaldehyde to yield methylene-imines which trimerize to trimethylenetriamine rings.[3] If urea were an amino acid amide, it could react with formaldehyde to form resins composed of trimethylenetriamine rings linked by methylene-bis bridges between amide groups on different rings. The reactions of amino acid amides and N-substituted amino acid amides with formaldehyde were investigated to test this theory.

Discussion

Glycinamide and ε-aminocaproamide react with aqueous formaldehyde at room temperature and in slightly acid solution to form gels. The composition of the resins after drying indicated that they were composed of trimethylenetriamine rings

linked by methylene-bis bridges between amide groups on different rings.

A substituent on the amine group of an amino acid amide would prevent polymer formation since two hydrogens on the amine group are necessary for the formation of trimethylene-triamine rings. Sarcosinamide did not react with formaldehyde to yield a resin.

Glycine methylamide has two hydrogens on the amino nitrogen and hence it should react with formaldehyde to yield trimethylenetriamine rings. If the lone hydrogen on the amide nitrogens would react with formaldehyde to yield methylene-bis linkages the reaction would lead to resins. Resins were not obtained, but rather the crystalline trimer of the methylene-imine derivative of glycine methylamide.

These experiments, coupled with investigations on substituted ureas which have shown that no substituted urea yields a polymer when treated with formaldehyde[4] makes it possible to present a new mechanism for the urea-formaldehyde reaction. The formation of resins from the reaction of urea and formaldehyde occurs because urea is an amino acid amide. The amine $-NH_2$ is converted to a methylene-imine group which trimerizes, and the amide $-NH_2$ reacts to give a methylene-bis amide, thus leading to cross-linked polymers. If either $-NH_2$ is substituted by even one R group, the polymerization is blocked.

The formation of resins from amino acid amides opens a new field of polymers which may have industrial importance. The amino acid amides can be modified so that a variety of polymers varying in hardness, extensibility, water resistance, etc. should be obtained.

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VITA

The author was born in Auburn, Nebraska on January 4, 1916. He attended the public schools of Sioux City, Iowa, graduating from East High School of that city in June, 1933. He attended Morningside College for two years and then transferred to Iowa State College where he received the degree of Bachelor of Science in Chemical Engineering in 1937. From 1937 to 1940 he was employed as a chemical engineer by the General Electric Company. He entered the Graduate School of the University of Illinois in the fall of 1940 and held teaching assistantships for two years and an Allied Chemical and Dye Corporation fellowship the third year.

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